2.4. CARBON MONOXIDE

2.4.1. MEASUREMENTS OF CARBON MONOXIDE

During 2000-2001 the study of the global distribution of CO in the lower troposphere continued using air samples collected through the CMDL Global Cooperative Air Sampling Network, in situ measurements at BRW and MLO, and air samples collected as part of the Measurement of Pollution in the Troposphere (MOPITT) validation program. Rates of drift in CMDL CO standards were quantified, and procedures for revision of the data were developed and implemented. In the air sampling network, the conversion on the last flasks to glass pistons with Teflon O-rings allowed CO to be measured at all active sites in the network. In situ measurements at BRW and at MLO each had unique problems. Improvements to the ruggedness of the air sampling units used aboard aircraft provided much greater success in vertical profiles at remote sites. The four vertical air sampling sites established for the validation of MOPITT provided monthly to biweekly profiles. Profiles were also determined over southern Africa as part of the Southern Africa Fire-Atmosphere Research Initiative 2000 (SAFARI 2000).

Flask Measurements

Provisional annual mean CO mole fractions for 2000 and 2001 are presented in Table 2.3. These values represent a correction to the CMDL CO scale (described in section 2.4.2). As discussed previously [*Novelli et al.*, 1998a], a high degree of interannual variation occurs in tropospheric CO (Figure 2.16). The sharp decline in global CO during 1992 has been attributed to the effects of the June 1991 eruption of Mt. Pinatubo [*Bekki et al.*, 1994], and as the effects of the eruption diminished in 1993, CO returned to previous levels. CO mole fractions determined in flask samples showed strong enhancements beginning late 1997 through 1998. In the southern hemisphere the anomaly was largely confined to the tropics during late 1997, when strong fires in Indonesia burned agricultural areas, forests, and peat swamps. In the northern hemisphere a weak summer minimum in 1998 was followed by high CO values throughout the fall. The enhanced CO is attributed to extreme and widespread forest burning during the summer and fall of 1998. Fires in Siberia detected by Advanced Very High Resolution Radiometer (AHVRR) burned late into the autumn. Interannual variations in the CO time series are probably related to variations in large-scale biomass burning. *Wotawa et al.* [2002] reported that two-thirds of the interannual CO variability in the extratropical northern hemisphere can be explained by boreal biomass burning. Measurements from the air sampling network show that after the high CO observed during 1997 and 1998, mixing ratios returned to pre-1998 levels in 2000 and 2001 (Figure 2.16).

In Situ Measurements

Quasi-continuous measurements of CO (3-4 samples per hour) continued at BRW and MLO. Both sites had minor problems. The instrument at BRW was off line during mid-
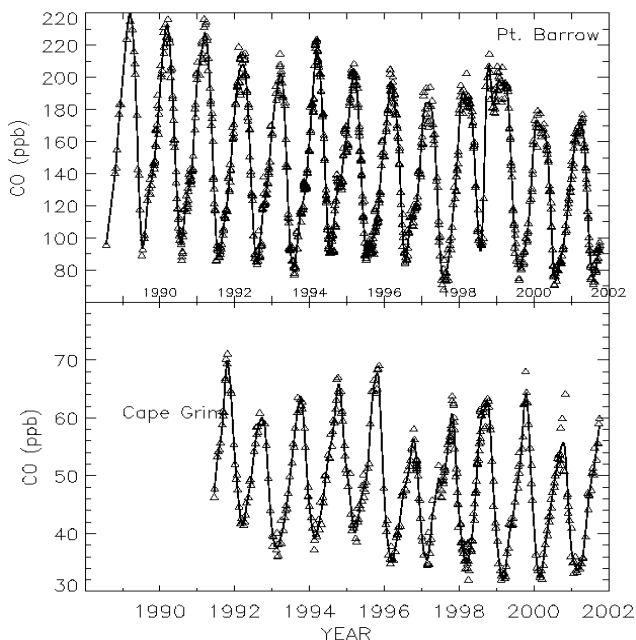

Fig. 2.16. Time series of tropospheric CO mixing ratios from Pt. Barrow, Alaska, and Cape Grim, Tasmania. Triangles are the mean of a pair of flasks; the solid curves are smooth fits to the data.

September-November 2000 because of a loss of standards during shipping. Measurements at MLO were hindered by a series of bad Hg lamps in the instrument, which often limited acceptable data to 1-2 samples per hour. In spite of these problems, CO determined from the in situ instruments agreed well with flask samples. At MLO the annual mean CO mole fractions determined from flask measurements and from the in situ instrument (selected for downslope conditions) agreed well, even during periods when the instrument's Hg lamp was marginal. High correlation between the flask and in situ measurements was found at both sites, and there is no significant offset between the two measurements (Figure 2.17). However, the scatter is greater at MLO than at BRW ($r = 0.973$ and 0.997, respectively).

The residuals from a function approximating the annual oscillations and trend [*Thoning et al.*, 1989] were used to examine CO at BRW. Using a transport model and estimates of emissions from fires burning in eastern Russia, *Bruhwiler et al.* (in preparation, 2002) showed that the high levels of CO seen at BRW during fall 1988 are consistent with the transport of emissions from fires in eastern Russia.

Vertical Profiles

With funding from the NASA Earth Enterprise System (formally the Earth Observing System), CMDL established four sites where the vertical profiles of CO and CH_4 are determined on a regular basis (Table 2.5). The measurement program has two goals: (1) It will provide vertical distributions of CO and CH_4 for the validation of MOPITT radiances and mixing ratios. MOPITT is a nadir-viewing, gas filter correlation radiometer that determines
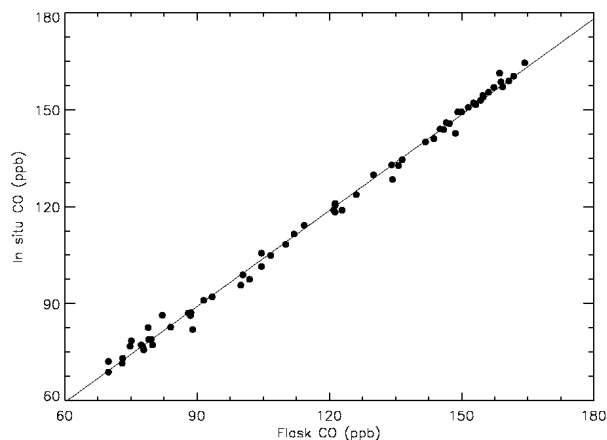
(a)
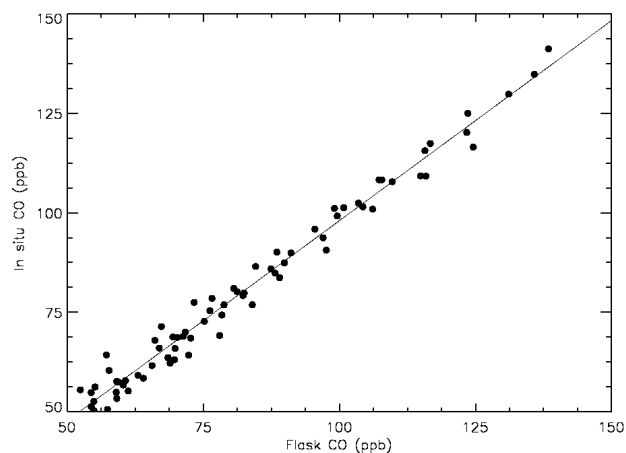
(b)

Fig. 2.17. Comparison of flask to in situ measurements at (a) Pt. Barrow and (b) Mauna Loa. The relationship between these measurements is defined with an orthogonal linear regression. BRW: $y = 0.087 \ (\pm 0.987) + 0.989 \ (\pm 0.008) \ x$; MLO: $y = -2.583 \ (\pm 1.485) + 1.006 \ (\pm 0.017) \ x$.

the column distribution and total abundance of CO and column abundance of CH_4. (2) It will use these data to better understand the distributions of trace gases above the boundary layer and provide additional constraints on trace gas budgets. The data collected by this program provide a unique view of CO and other trace gases as a function of altitude.

The portable air sampling equipment developed at CMDL is used on chartered aircraft to collect air samples at altitudes of up to 8 km above sea level once or twice per month. Flights are scheduled such that the aircraft is about halfway through its descent as the satellite passes overhead. Analysis in Boulder includes the suite of gases measured by CCGG: CO and CH_4, and also CO_2, H_2, N_2O, and SF_6. In addition to the long-term sites, profiles were measured over South Africa, Botswana, and the western Indian Ocean as

Table 2.5. MOPITT Validation Sites

Site	Latitude/ Longitude	Maximum Altitude (km)	Environment
Poker Flats, AK	65.1ºN/147.5ºW	7.5	HNH background continental
Harvard Forest, MA	42.5ºN/71.2ºW	7.9	NH polluted continental
Molokai, HI	21.4ºN/157.2ºW	7.9	Background NH oceanic
Rarotonga, Cook Islands	21.2ºS/159.8ºW	5.0	Background SH oceanic
Southern Africa*	20–30ºN/22–35ºE	8.4	SH background and polluted oceanic and continental

*SAFARI 2000 campaign (not a permanent site).

part of the SAFARI 2000 campaign. Preliminary comparison of the CMDL profiles with the MOPITT retrievals are within the MOPITT specifications. Other flights in Colorado, Oklahoma, California, and South Africa were used to validate measurements made by two MOPITT simulators developed at the University of Toronto and at the National Center for Atmospheric Research/Atmospheric Chemistry Division (NCAR/ACD). More than 110 flights were conducted as part of this program. Regular sampling at the four MOPITT sites builds time series that define the trends and seasonal cycles of CO and the other trace gases at altitude (Figure 2.18).
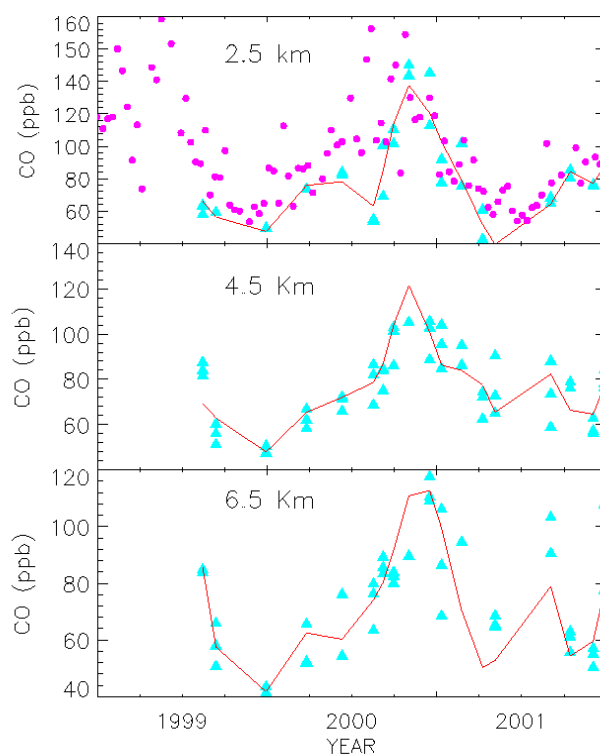

Fig. 2.18. CO time series from Molokai, Hawaii, binned for each 1000 ± 500 m altitude (typically 2-3 samples; each sample is plotted as a solid triangle). In the top panel, open circles are the flask results from MLO.

2.4.2. CO REFERENCE GASES

Nine CO standards were prepared by CMDL using gravimetric methods during late 1999 and early 2000. Mole fractions assigned to CMDL working standards referenced against the new gravimetrics were significantly larger than those previously assigned based upon the original CMDL CO scale [*Novelli et al.*, 1991, 1994]. Mole fractions assigned to the working standards using dynamic dilution of a National Institute of Standards and Technology (NIST) 9.7-ppm standard in 2000 confirmed the higher CO levels in the new standards. Although frequent intercomparison of a suite of standards maintained at CMDL did not suggest drift in the standards, comparison of calibrations of working standards referenced to three sets of gravimetric standards (prepared in 1989/1992, 1996, and 1999/2000) did indicate a change over time. A re-evaluation of the CO scale, extending back to the first set of gravimetric standards, plus confidence in both the original scale and the 1999/2000 gravimetric standards, lead to the belief that both the secondary and working standards have changed over time. Calculation of linear drift rates of ±0.3 ppb yr^{-1} between 1992 and 1999/2000 are consistent with the results from a set of gravimetric standards prepared in 1996, and with comparisons with several other laboratories [*Novelli et al.*, 1998b; *Masarie et al.*, 2001]. Thus, there is consistent evidence that many of the CMDL standards have drifted upward.

Calibration procedures were based upon the analysis of six to eight standards with mixing ratios between 50 and 200 ppb; calibration curves were generated using area response and the CO mixing ratio assigned to the standards. Their relationship was defined using both a quadratic and third-order polynomial curve [*Novelli et al.*, 1998a]. The original set of working standards used between 1990 and mid-1997 were all calibrated against the 1992 and the 1999/2000 gravimetric standards, and in many cases also against the gravimetric standards prepared in 1996. From calibrations, a rate of change in the working standard was determined. These rates were then applied to the mole fraction assigned to each standard in 1992, and new calibration curves were generated. Combined with the archived sample area responses, each sample analyzed through June 1997 was assigned a new mole fraction. (In mid-1997 the CO analytical system was changed to the Measurements of Atmospheric Gases Influencing Climate Change (MAGICC) system, and a second set of working standards was installed.)

All CO calibrations for high-pressure cylinders (standards), which were also made against the original set of working standards, required revision. A similar approach to that described above for flask measurements was used for the cylinders. First, the calibration curves were re-calculated based upon the corrected standard CO values. Archived responses from the calibrations were then combined with the revised curves to assign new CO mole fractions to the standards. The set of working standards used on MAGICC were corrected, and the sample CO value was recalculated. Table 2.6 compares revised mole fractions of several standards (calculated as described above) to mole fractions determined by direct calibration using the 1999/2000 gravimetric standards as the reference. A histogram of the differences between mixing ratios assigned to a number of tanks during 2000 and mixing ratios calculated by the correction procedure (Figure 2.19) shows that the calculated CO mixing ratios determined by the correction are generally somewhat greater than those measured. The mean bias of the corrected mole fractions is −0.9% (0.8 ppb) relative to the measured mole fractions. The tendency toward more negative differences is shown in the negative skewness (−0.71). This offset suggests that the rates of drift assigned to the working standards may, in general, have been overestimated by 0.1-0.2 ppb yr^{-1}.

TABLE 2.6. Comparison of Measured and Revised CO Mixing Ratios

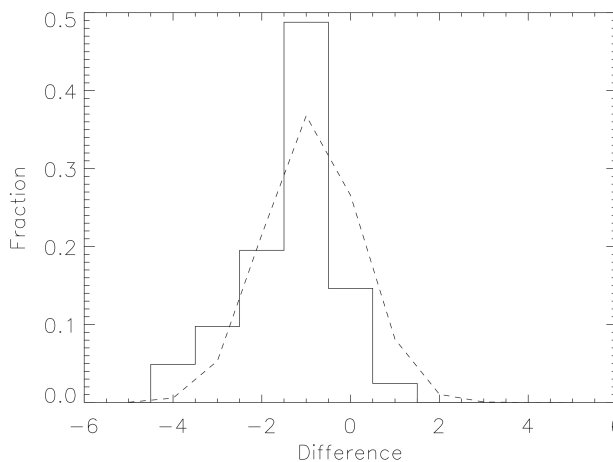| Tank ID	Measured CO (ppb)	Calculated CO (ppb)
104208	49.1 (0.4)	49.5 (0.5)
01790	54.0 (0.7)	54.7 (0.8)
01783	69.2 (1.0)	71.2 (0.8)
71607	140.8 (0.8)	141.7 (1.3)
68734	167.4 (0.6)	168.5 (0.8)
38734	200.6 (1.1)	202.4 (1.7)

Values in parentheses are 1σ of the mean.

Fig. 2.19. Histogram of the difference between CO mole fractions assigned to standards by measurement and the 1999/2000 gravimetric standards and mole fractions assigned by the data revision procedure. CMDL working standards used in the correction are not included. The dashed curve is a Gaussian fit to the data.